

Supramolecular guests in solvent driven block copolymer assembly: From structured nanoparticles to micelles

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Supporting information

Experimental

Materials

All reagents were purchased from Sigma Aldrich unless otherwise specified. Dry THF was used directly from a solvent purification system.¹ Styrene was stirred over CaH₂ and degassed through three freeze-pump-thaw cycles, followed by distillation from dibutyl-magnesium to a flame-dried buret immediately prior to use. 2-vinyl-pyridine was stirred and degassed over triethylaluminum, and distilled to a flame-dried buret immediately prior to use. Water was purified using a millipore water purification system.

Polymer synthesis

Burets containing dry THF, purified styrene, and purified 2-vinyl-pyridine were attached to a flame-dried reactor under an argon atmosphere. The reactor assembly was again flame-dried and cycled between vacuum (5 mTorr) and a positive-pressure argon atmosphere five times. Under an argon atmosphere, THF was added and the reactor temperature was decreased to $-70\text{ }^{\circ}\text{C}$. Styrene was added to the reactor followed by a predetermined amount of sec-butyllithium initiator (1.4M in hexane). Polymerization of styrene was allowed to proceed for 1.5h, 2-vinylpyridine was then added and polymerization continued for an additional 1.5h. The polymerization was terminated with degassed isopropanol. The PS-*b*-P2VP was precipitated in hexanes, filtered, and dried in vacuo. ^1H NMR spectroscopy: $M_n = 19\text{ kDa}$, $X_{\text{P2VP}} = 25\%$. Size-exclusion chromatography relative to PS-standards: PDI = 1.13

Self-assembly of BCP into nanoparticles

The block copolymer was dissolved in THF (4.5 mL, 0.1 wt %) and the solution was continuously stirred while water was added (9mL @ 1 mL/min). The solution was then allowed to stand under ambient conditions to evaporate THF (typically 3 days).

For supramolecular systems the BCP was dissolved in THF (10 mg/ml) and equimolar (relative to PVP block) addition of guest was added and stirred at room temperature for 12 hours. This solution was then diluted with THF (0.1 wt %) and the above self assembly procedure was followed. To remove PDP the particle dispersion was centrifuged (1000g, 15 min) and dispersed in methanol and stirred for 2 h. The dispersion was then isolated by multiple centrifugation dispersion cycles in methanol.

Characterization

Transmission electron microscopy was conducted on a FEI-T20 instrument, operating at 200 kV. Grids were prepared by casting a concentrated dispersion of particles onto the copper grids and the droplet was wicked through the grid using tissue paper. Particle dispersions were cast onto freshly cleaned silicon wafers, coated with a gold layer and visualized using Scanning electron microscopy (SEM) on a FEI XL30 Sirion FEG microscope.

Dynamic light scattering measurements were performed on a Wyatt DynaPro NanoStar instrument using Dynamics 7.0 software. Data were collected at 25 °C with an acquisition time of 5 sec. Hydrodynamic radii were averaged over 20 acquisitions. Solvent refractive index values were calculated based on volume composition from independent measurements on aqueous THF solutions performed on a Wyatt Optilab rEX instrument. Viscosities of the binary solvent mixtures were calculated from previously reported data.²

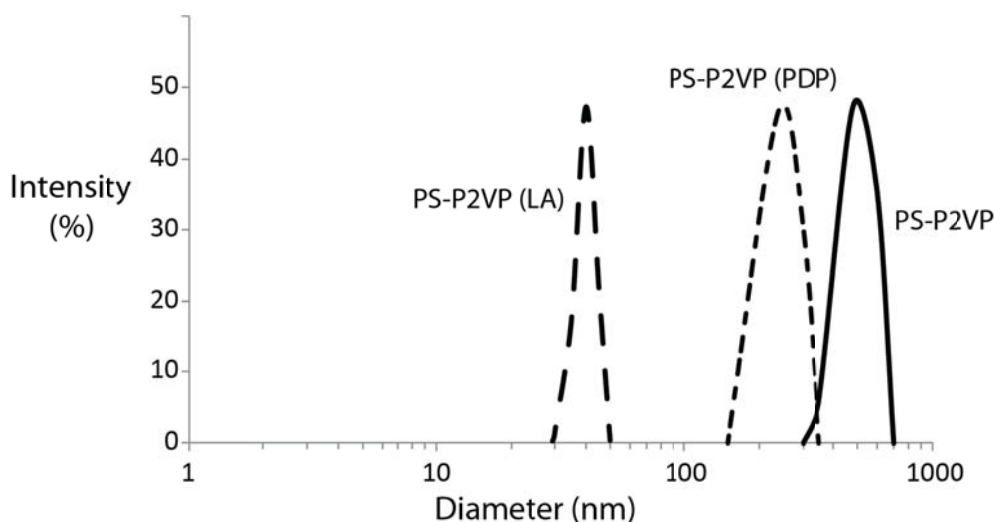


Figure S1 – Dynamic light scattering data for the different assemblies. **PS-P2VP** – the pure block copolymer assembled into water from THF, showing BCP particles of around 500nm diameters. **PS-P2VP (PDP)** – the supramolecular assembly of pentadecyl phenol and PS-P2VP assembled into water from THF, showing BCP supramolecular particles of around 250nm diameters. **PS-P2VP-(LA)** - the

supramolecular assembly of PS-P2VP with lactic acid assembled into water from THF, showing traditional micelles of 40nm diameters.

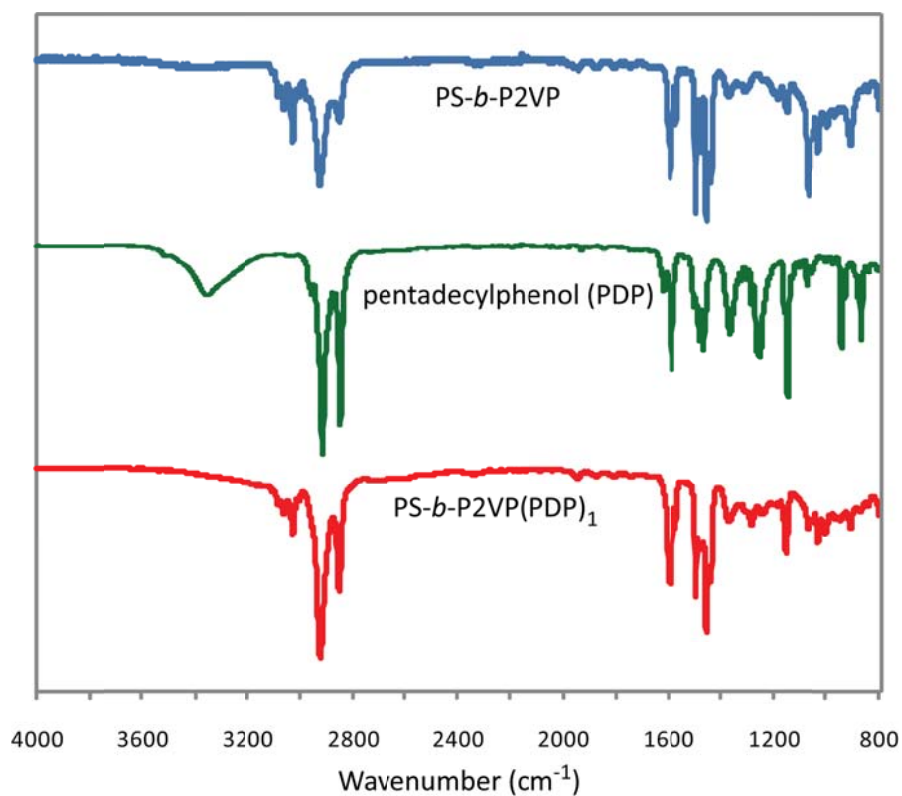


Figure S2 – full FTIR spectrum of (a) pure block copolymer, (b) pentadecyl phenol , and (c) supramolecular complex.

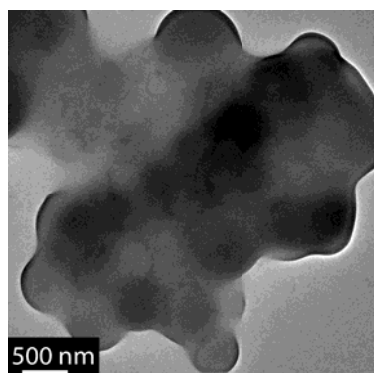


Figure S3 – TEM of control experiment, self-assembly of pentadecyl phenol without block copolymer.

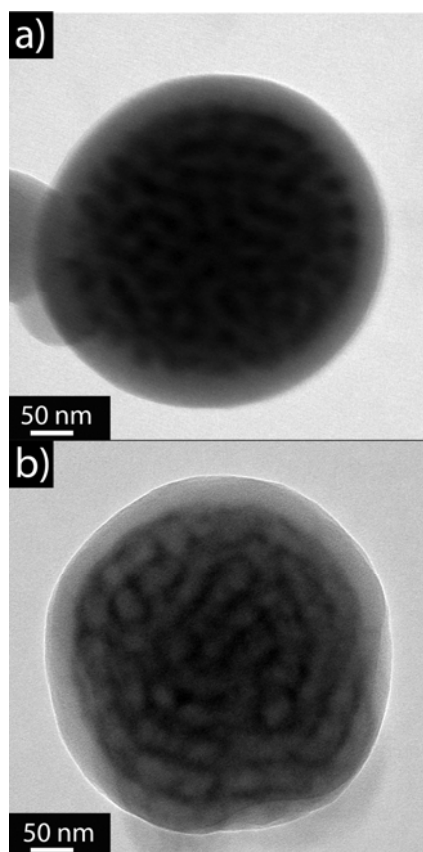


Figure S4. TEM micrographs of assemblies with varying incorporation of hydrophobic guests. a) PS-b-P2VP (PDP)_{0.3}. b) PS-b-P2VP (PDP)_{0.4}

¹ Pangborn, A. B.; Giardello, A. Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organomet.* **1996**, *15*, 1518.

² Aminabhavi, T. M.; Gopalakrishna, B. *J. Chem. Eng. Data*, **1995**, *40*, 856-861.